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Kinetics of the Gas-Phase Thermal Bromination of Acetone. Heat of Formation and Stabilization Energy of the Acetonyl Radical[1a]

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Abstract: The gas-phase thermal bromination of acetone has been studied spectrophotometrically over the temperature range 221–345°. The pressure of acetone was varied from 2 to 223 Torr and of Br_2 from 3 to 195 Torr. Above 252°, the kinetics conform to the mechanism $Br_2 \rightleftarrows 2Br$, $Br + CH_3COCH_3 \rightleftarrows CH_3CO\dot{C}H_2 + HBr$ [(1) forward, (2) reverse], $CH_3CO\dot{C}H_2 + Br_2 \rightarrow CH_3COCH_2Br + Br$ (3). From measurements of initial rates, $\log (k_1/M^{-1}\ \sec^{-1}) = (11.0 \pm 0.22) - (13.9 \pm 0.6)/\theta$, where $\theta = 2.303RT$ in kcal/mol. Inhibition by added HBr was investigated and the ratio k_2/k_3 is given by $\log (k_2/k_3) = (-0.64 \pm 0.41) - (1.8 \pm 1.1)/\theta$. The results, combined with the assumption that $E_3 = 1 \pm 1$ kcal/mol, lead to $\Delta H_f{}^\circ{}_{298}(CH_3CO\dot{C}H_2) = -5.5 \pm 1.8$ kcal/mol and $DH^\circ{}_{298}(CH_3COCH_2\text{–}H) = 98.3 \pm 1.8$ kcal/mol. These values agree well with previous estimates obtained from iodination studies and confirm the conclusion that there is no resonance stabilization in the acetonyl radical due to conjugation of the radical site. The C–H bond strength in acetone is the same as that in ethane, but the value of A_1 is significantly lower than that for the corresponding reaction involving ethane and this difference is accounted for in terms of transition-state theory.

The stabilization energy in the allyl radical due to delocalization of the unpaired electron may be defined as $DH^\circ{}_{298}(n\text{-}C_3H_7\text{–}H) - DH^\circ{}_{298}(\text{allyl–H})$. The value is $\sim$10 kcal/mol.[2a] Measurements have also been made[2b] on other hydrocarbon radicals in which conjugation of the radical site is possible, *e.g.*, methylallyl, pentadienyl, and benzyl. However, until recently, there were very few data on stabilization energies in β-carbonyl radicals. From an analysis of the Arrhenius parameters for the decompositions of cyclobutyl ketones in terms of a biradical mechanism, the stabilization energy in the methylacetonyl radical has been estimated as 7.7 ± 2 kcal/mol.[3] Grzechowiak, Kerr, and Trotman-Dickenson[4] have measured the activation energies for the abstraction of hydrogen atoms by $\dot{N}F_2$ radicals from acetone and some hydrocarbons and, from a Polanyi relationship, they arrive at $DH^\circ(CH_3COCH_2\text{–}H) = 92 \pm 3$ kcal/mol.[5] This bond dissociation energy, when compared with $DH^\circ(n\text{-}C_3H_7\text{–}H)$, leads to a value of 6 ± 3 kcal/mol for the stabilization energy in the acetonyl radical. The difference between acetonyl and methylacetonyl is in accord with the difference between allyl and methylallyl.[2b]

Unfortunately, the above value for $DH^\circ(CH_3COCH_2\text{–}H)$ is suspect since the Polanyi type of relationship is only applicable to reactions of atoms or radicals with a series of compounds of the same class.[6] More-

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[1] (a) This work was supported in part by Grant No. AP-00353-05 from the Air Pollution Control Administration, Public Health Service; (b) Post-Doctoral Research Associate.

[2] (a) D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2136 (1969); (b) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

[3] H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

[4] J. Grzechowiak, J. A. Kerr, and A.F. Trotman-Dickenson, *Chem. Commun.*, 109 (1965); *J. Chem. Soc.*, 5080 (1965).

[5] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

[6] S. W. Benson and W. B. DeMore, *Annu. Rev. Phys. Chem.*, **16**, 297 (1965).

over, recent measurements of the primary C–H bond strength in acetone[7] and the secondary C–H bond strength in methyl ethyl ketone[8] by the iodine-atom technique[2b] have shown that the stabilization energy in the acetonyl radical is zero and that in methylacetonyl is 2.7 kcal/mol. These values imply that a concerted mechanism must make a significant contribution to the decomposition of cyclobutyl ketones. The results for the iodination of methyl ethyl ketone are clear-cut, but those for acetone are somewhat less reliable owing to the occurrence of heterogeneous processes.[7] Therefore, an independent check on $DH°_{298}(CH_3COCH_2\text{–}H)$ seemed desirable. Since bromination studies have, in general, yielded reliable values for C–H bond strengths,[9] we have sought to measure $DH°_{298}(CH_3COCH_2\text{–}H)$ from a study of the direct thermal bromination of acetone using spectrophotometric techniques which have proved to be highly successful in iodination studies.[10]

Experimental Section

Materials. Spectroscopic grade acetone (Eastman) was degassed and fractionated in the vacuum line until gas chromatographically pure. Reagent grade bromine (Allied Chemicals) was treated with KBr to remove chlorine. Anhydrous HBr from Matheson was purified by vacuum distillation. Both acetone and bromine were repeatedly degassed at liquid nitrogen temperatures prior to each experiment. Bromoacetone (Columbia Chemicals) was obtained as a black liquid. Vacuum distillation yielded a clear, oily liquid which rapidly darkened under the influence of heat and light, and then slowly solidified. The material could not be quantitatively distilled into the reaction vessel, and therefore only qualitative measurements of ultraviolet spectra were possible. However, the spectra of gas-phase bromoacetone in the quartz reactor remained unchanged under conditions similar to those in the reaction studies.

Apparatus. Reaction rates were determined from the rate of disappearance of Br_2 measured spectrophotometrically. The apparatus, which is the same as that used for iodine-atom reactions, has been described in detail previously.[10] Reactions occurred in a cylindrical quartz vessel, enclosed in an electrically heated aluminum block furnace, and situated above the sample compartment of a modified Cary Model 15 spectrophotometer. A conventional high-vacuum system was attached and pressures were measured with a Pace pressure transducer used as a null device. A packed vessel (surface-to-volume ratio greater by a factor of 8 than that of the unpacked vessel), specially designed for this type of apparatus, has already been described.[11]

Procedure. This spectrophotometric technique has proved to be highly sensitive and very accurate for iodine systems, and this is the first time that it has been applied to bromination studies. The spectrophotometer was calibrated with known pressures of Br_2 measured at the run temperature. A plot of optical density (at 415 nm) against Br_2 pressure was linear up to 15 Torr over the entire temperature range of this investigation. When Br_2 pressures greater than 15 Torr were used it was necessary to calibrate at 550–600 nm. However, at the higher pressures, plots of optical density *vs.* Br_2 pressure were curved, and when such pressures were used in kinetic runs the measured time variation of optical density was corrected accordingly. No other species in this reaction system absorbed in the same wavelength region as Br_2.

In a run, Br_2 was admitted to the reaction vessel and the pressure and absorbance were measured. The synchronous chart drive was started at a desired speed and acetone was then admitted at a pressure obtained from the total pressure and the Br_2 pressure. Reaction began at once and the absorbance–time trace was smooth. Mixing was virtually instantaneous except at the lower temperatures (<250°). However, at these temperatures the reaction rate was slow enough for the mixing time to be short when compared with the time for any single run. The order of introduction of reactants into the reaction vessel had no effect upon the reaction rate. In most cases, Br_2 was added to acetone because its initial pressure could then be conveniently measured spectrophotometrically, and in this way accurately controlled variations in both $[Br_2]_0$ and $[CH_3COCH_3]_0$ could be obtained. It was verified several times that the spectrophotometer light beam was too weak to initiate any photochemical reaction.

At the end of a run the final pressure was measured by backing helium, at the initial reaction pressure, up to the reactor stopcock, opening it, and observing any pressure change on the pressure transducer. In this way ΔP could be measured to 0.1 Torr. The contents of the reaction vessel were collected for analysis by condensation into a liquid-nitrogen-cooled trap. Gas chromatographic analysis for bromoacetone was unsuccessful owing to the instability of the compound. However, the ultraviolet spectra of reaction products, after allowing for absorption due to HBr and acetone, were similar to that of a qualitative sample of bromoacetone.

Results

The overall reaction is expected to be

$$Br_2 + CH_3COCH_3 \rightleftarrows CH_2COCH_2Br + HBr \qquad (A)$$

No traces of noncondensable gases could be detected and there was no pressure change during the reaction. The formation of CH_3COCH_2Br was confirmed only qualitatively, but there was no evidence to indicate that the stoichiometry is other than (A).

It was found that the initial rate of disappearance of Br_2, $-(d[Br_2]/dt)_i$, was first order in acetone and one-half order in Br_2, except at temperatures below 250°, where the order in Br_2 shifts to ~0.8. Order dependence and reaction rates, including those at the lowest temperatures, were essentially unchanged in a packed vessel. Since there is little surface catalysis, this shift in rate law with decrease in temperature is probably due to a change in reaction mechanism.

The initial rate measurements made in the temperature range 260–345° were interpreted in accordance with the following mechanism, which is similar to that for other thermal bromination systems[9]

$$Br_2 \rightleftarrows 2Br \qquad K_{Br_2}$$

$$Br + CH_3COCH_3 \underset{2}{\overset{1}{\rightleftarrows}} CH_3CO\dot{C}H_2 + HBr$$

$$CH_3CO\dot{C}H_2 + Br_2 \xrightarrow{3} CH_3COCH_2Br + Br$$

A steady-state treatment gives

$$-\frac{d[Br_2]}{dt} = \frac{k_1K_{Br_2}^{1/2}[Br_2]^{1/2}[CH_3COCH_3]}{1 + k_2[HBr]/k_3[Br_2]} \qquad (B)$$

In the initial stages, when no HBr is present, (B) reduces to

$$-(d[Br_2]/dt)_i = k_1K_{Br_2}^{1/2}[Br_2]^{1/2}[CH_3COCH_3] \qquad (C)$$

It has been suggested[12] that termination processes other than

$$Br + Br + M \longrightarrow Br_2 + M$$

may be important in thermal bromination systems, so that the steady-state concentration of bromine atoms is no longer controlled by the thermodynamic equilib-

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[7] R. K. Solly, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, 2, 11 (1970).

[8] R. K. Solly, D. M. Golden, and S. W. Benson, submitted for publication.

[9] (a) J. W. Coomber and E. Whittle, *Trans. Faraday Soc.*, **63**, 2656 (1967); (b) J. C. Amphlett and E. Whittle, *ibid.*, **64**, 2130 (1968).

[10] (a) D. M. Golden, R. Walsh, and S. W. Benson, *J. Amer. Chem. Soc.*, 87, 4053 (1965); (b) R. Walsh and S. W. Benson, *ibid.*, **88**, 3480 (1966).

[11] S. W. Benson, F. R. Cruickshank, and R. Shaw, *Int. J. Chem. Kinet.*, **1**, 29 (1969).

[12] S. W. Benson and J. H. Buss, *J. Chem. Phys.*, 28, 301 (1958).

Table I. Kinetic Data for the Reaction $Br + CH_3COCH_3 \rightarrow CH_3CO\dot{C}H_2 + HBr$

Temp, °C	$[Br_2]_0$, Torr	$[CH_3COCH_3]_0$, Torr	$-10^2(d[Br_2]/dt)_i$, Torr/sec	$10^5 K_{Br_2}{}^{1/2}$,[a] Torr$^{1/2}$	$10^{-5}k_1$, M^{-1} sec^{-1}
345.0	2.8	13.78	7.90		11.75
345.0	6.65	25.5	20.2		10.52
345.0	11.0	14.1	15.8	11.22	11.49
345.0	5.7	11.28	8.78		11.18
345.0	5.7	6.68	4.65		9.93
326.5	2.6	28.8	6.18		7.95
326.5	5.8	18.65	6.98		9.20
326.5	14.7	14.65	8.36	6.31	9.05
326.5	11.3	19.7	9.28		9.27
326.7	15.0	75.0	42.4		8.68
319.2	8.1	42.7	11.01		7.04
319.2	18.0	42.6	15.75		6.72
319.3	3.7	41.7	7.08	4.79	6.80
319.1	34.5	44.3	25.0		7.40
319.0	116.5	43.8	50.0		8.12
308.6[b]	14.5	44.0	10.3		6.40
308.8[b]	32.8	42.8	16.6	3.47	7.05
308.9[b]	54.6	43.8	19.9		6.40
302.6	60.0	80.0	29.3		6.03
302.5	12.7	65.5	12.4		6.75
302.5	21.3	222.7	41.8		5.18
302.6	6.23	5.12	0.643		6.34
302.6	10.8	5.05	0.885		6.76
302.3	11.42	44.4	5.16		4.38
302.3	13.12	94.4	11.12		4.18
302.3	6.4	100.6	7.96		4.00
302.5	3.04	50.5	3.26		4.72
302.5	13.05	12.4	2.26		6.38
302.5	11.75	18.15	2.10		4.31
302.5	12.25	1.67	0.303	2.82	6.60
302.3	12.32	6.96	0.971		5.08
302.3	12.32	11.28	1.23		3.97
302.3	11.92	39.4	3.87		3.84
302.5	4.1	27.1	2.20		4.92
302.5	4.2	27.4	2.20		4.99
302.4	4.8	27.6	2.07		4.34
302.3	8.5	27.8	3.34		5.26
302.3	12.5	28.2	3.87		4.96
302.5	29.0	27.4	7.37		6.35
302.5	82.0	28.2	12.54		6.25
302.1	141.0	27.9	14.5		5.58
302.1	195.0	27.2	17.8		5.98
285.4	4.85	18.25	0.72		4.20
285.4	5.10	32.2	1.08		3.50
285.4	13.0	47.9	2.60	1.48	3.53
285.3	13.2	26.7	1.58		3.83
285.3	9.7	31.1	1.58		3.84
285.1	25.7	99.0	67.3		3.36
261.8	8.0	38.8	0.414		1.73
261.8	10.7	47.3	0.621		1.85
261.8	5.45	36.3	0.414	0.724	2.24
261.8	10.0	33.9	0.462		1.97
261.8	6.7	114.5	1.19		1.85
261.8	5.45	35.6	0.345		1.91
259.5[b]	65.3	41.7	1.49		2.70
259.5[b]	17.0	41.7	0.68	0.55	2.40
259.4[b]	10.0	41.2	0.57		2.66
259.5[b]	48.6	43.3	1.41		2.82
251.3[c]	113.5	43.1	1.56		2.95
251.3[c]	52.5	42.3	1.00	0.38	2.72
251.3[c]	6.75	42.8	0.242		1.85
242.2[c]	12.15	86.8	0.387		1.63
242.3[c]	6.2	44.8	0.147		1.68
242.3[c]	11.4	45.6	0.206	0.251	1.72
242.3[c]	9.2	21.4	0.093		1.84
242.3[c]	12.0	35.8	0.160		1.65
225.0[b,c]	35.2	45.3	0.148		1.48
224.5[b,c]	59.3	45.7	0.186		1.42
224.5[b,c]	17.0	45.9	0.113	0.118	1.73
224.5[b,c]	8.6	43.2	0.062		1.30
222.3[c]	10.4	44.1	0.063		1.34
220.9[c]	5.85	44.6	0.044		1.26
220.3[c]	12.6	39.5	0.047		1.18
221.0[c]	6.3	41.8	0.047		1.75
221.4[c]	120.0	41.7	0.272	0.100	2.32
221.4[c]	86.5	42.2	0.294		2.08
221.3[c]	56.5	42.3	0.214		1.81
221.0[c]	25.5	42.2	0.125		1.39

[a] K_{Br_2} is the equilibrium constant for $Br_2 \rightleftarrows 2Br$, calculated from: D. R. Stull, Ed., "JANAF Interim Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1963. [b] Packed vessel experiments. [c] Rate $\propto [Br_2]^x$, where $x \sim 0.8$; k_1 is k_1(app) $\propto [Br_2]^{x-0.5}$.

Table II. Kinetic Data for Inhibition by HBr

Temp, °C	$[Br_2]_0$, Torr	$[CH_3COCH_3]_0$, Torr	$[HBr]_0$, Torr	$-10^2(d[Br_2]/dt)_i$, Torr/sec	$\frac{k_1[Br][CH_3COCH_3]}{-d([Br_2]/dt)_i}$	k_2/k_3
345.0	14.25	10.0	193.5	8.40	1.550	0.0405
345.0	6.2	11.38	154.1	3.68	2.560	0.0626
345.0	6.8	43.7	65.5	24.6	1.600	0.0625
326.5	3.8	19.1	78.9	2.74	1.992	0.0477
302.2	6.1	29.4	78.1	1.98	1.475	0.0372
302.2	2.81	29.0	39.0	1.18	1.652	0.0468
302.3	4.2	10.25	53.3	0.46	1.825	0.0650
302.3	4.7	17.12	40.7	1.15	1.305	0.0352
285.3	11.1	67.5	133.9	2.31	1.465	0.0386
285.3	3.5	34.5	86.0	0.447	2.170	0.0476
285.1	3.7	32.8	59.7	0.608	1.565	0.0349
261.8	6.0	74.5	74.5	0.524	1.548	0.0442
261.8	5.5	24.5	109.0	0.138	1.858	0.0438
261.8	2.9	23.5	97.0	0.076	2.360	0.0408
261.8	7.7	20.9	86.6	0.173	1.495	0.0442

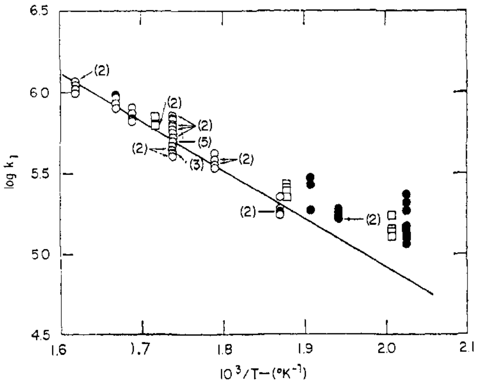


Figure 1. Arrhenius plot for the reaction Br + CH_3COCH_3 → $CH_3CO\dot{C}H_2$ + HBr: ●, not included in least-mean-squares estimate of line; □, packed vessel experiments. Numerals indicate overlapping points.

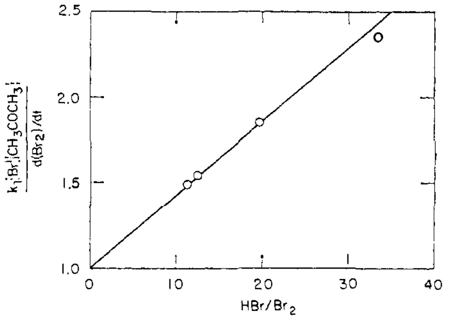


Figure 2. Plot showing the effect of inhibition by added HBr. k_1 is obtained from initial (uninhibited) data and the line is constrained to pass through the point (1,0).

rium, K_{Br_2}. In the present case, the most likely additional chain termination step is

$$CH_3CO\dot{C}H_2 + Br \xrightarrow{5} CH_3COCH_2Br$$

In the limit that reaction 5 is the sole contribution to chain termination, the rate should show a first-order dependence in Br_2. The order in acetone will remain at unity unless reaction 5 is termolecular. The present results indicate that reaction 5 is making a significant contribution to chain termination at temperatures below 250°.

Experimental results are listed in Table I, and k_1 was calculated from eq C. The least-squares Arrhenius plot (Figure 1) through only those data obtained in the unpacked vessel in the temperature range 263–345° is given by the equation

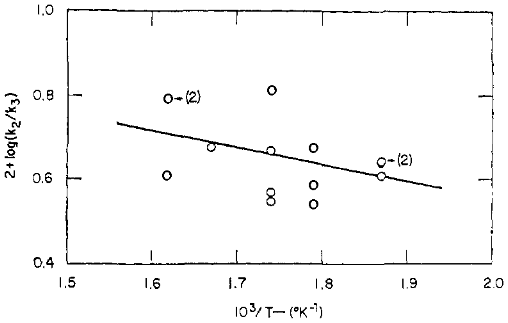


Figure 3. Arrhenius plot for the inhibition ratio, k_2/k_3.

$$\log (k_1/M^{-1}\ \text{sec}^{-1}) = (11.0 \pm 0.22) - (13.9 \pm 0.6)/\theta$$

The errors quoted are the standard deviations. Values of k_1 obtained in the packed vessel fall on the same straight line. The low-temperature (<252°) results do not fit the rate expression in (C), but values of an "apparent k_1" calculated on the assumption of rate law C are shown in Figure 1 for comparison.

If significant pressures of HBr are present in the initial stages of reaction, then eq B must be used. A series of HBr-inhibited runs was made and the experimental results are given in Table II. A plot of $k_1K_{Br_2}{}^{1/2}[Br_2]^{1/2}[CH_3COCH_3]/-(d[Br_2]/dt)_i$ *vs.* $[HBr]/[Br_2]$ is shown in Figure 2 for runs made at 262°. The line is constrained to pass through the point (1,0) and the value of k_1 used is that calculated from the Arrhenius equation given above. The inhibition ratio k_2/k_3 is ~0.04 for most bromination systems,[9b,13] and therefore its measurement by inhibition experiments and the use of eq B will be rather sensitive to errors in measuring $-(d[Br_2]/dt)_i$. From 15 runs in the range 262–345°, we obtain the Arrhenius plot in Figure 3, from which

$$\log (k_2/k_3) = (-0.64 \pm 0.41) - (1.8 \pm 1.1)/\theta$$

The errors quoted are the standard deviations estimated by least-squares analysis. This result is consistent with values of k_2/k_3 found for the thermal brominations of CF_3H[9b] and C_2F_5H.[9b]

(13) A. F. Trotman-Dickenson and G. S. Milne, "Tables of Bimolecular Gas Reactions," NSRDS-NBS9, National Bureau of Standards, U. S. Government Pirnting Office, Washington, D. C., 1967.

The absolute Arrhenius parameters for the reactions of $CH_3CO\dot{C}H_2$ with HBr and Br_2 are unknown, but a consideration of the available data[13] on k_2/k_3 and k_2/k_3' for the reactions

$$R\cdot + HBr \xrightarrow{2} RH + Br$$

$$R\cdot + Br_2 \xrightarrow{3} RBr + Br$$

$$R\cdot + I_2 \xrightarrow{3'} RI + I$$

suggests that, in general, $E_3 = 1 \pm 1$ kcal/mol (it is widely accepted that $E_3' = 0 \pm 1$ kcal/mol[2]). Moreover, a direct determination[14] of $E_3 = 0.7 \pm 0.5$ kcal/mol for

$$\dot{C}F_3 + Br_2 \longrightarrow CF_3Br + Br$$

supports this conclusion. Consequently, from our value of $E_2 - E_3 = 1.8 \pm 1.1$ kcal/mol, we estimate that for

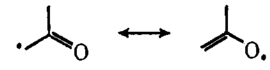
$$CH_3CO\dot{C}H_2 + HBr \xrightarrow{2} CH_3COCH_3 + Br$$

$E_2 = 2.8 \pm 1$ kcal/mol. This is consistent with values of E_2 for $R\cdot = \dot{C}H_3$ (1.4),[15] $\dot{C}F_3$ (2.8),[9b] $\dot{C}_2H_5$ (2.3),[15] and $\dot{C}_2F_5$ (3.9).[9b] Thus, for reaction 1, $\Delta H_{576} = 11.1 \pm 1.2$ kcal/mol. $C_p°(CH_3CO\dot{C}H_2)$ may be estimated[16] by comparison with $C_p°(CH_3COCH_3)$, and in conjunction with known values of $C_p°(Br)$ and $C_p°(HBr)$ this gives $\overline{\Delta C_p°}$(reaction 1) $= (\Delta C_p°_{576} + \Delta C_p°_{298})/2 = 1.0 \pm 2$ gibbs/mol, so that $\Delta H°_{298} = 10.8 \pm 1.8$ kcal/mol. From the known heats of formation of the other species,[16] $\Delta H_f°_{298}(CH_3CO\dot{C}H_2) = -5.5 \pm 1.8$ kcal/mol, and therefore $DH°_{298}(CH_3COCH_2\text{–}H) = 98.3 \pm 1.8$ kcal/mol.

Discussion

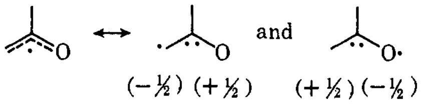
Solly, Golden, and Benson[7] have measured the rate of reaction of I_2 with acetone and, from a study made difficult by surface effects, they concluded that $DH°_{298}(CH_3COCH_2\text{–}H) = 98 \pm 2.6$ kcal/mol and thus $\Delta H_f°_{298}(CH_3CO\dot{C}H_2) = -5.7 \pm 2.6$ kcal/mol. Our bromination work, which was uncomplicated by heterogeneous processes, confirms these values. The only significant difference is the reduction in error limits. The discrepancy between the values reported by Grzechowiak, Kerr, and Trotman-Dickenson[4] and those obtained from iodination and bromination studies suggests that studies of $\dot{N}F_2$ radical reactions may not be a reliable technique for the estimation of C–H bond energies. Further evidence in support of this conclusion may be obtained from a comparison of the values for the C–H bond energy in cyclopentane. The $\dot{N}F_2$ radical technique gives 92.4 kcal/mol,[4] whereas the iodine-atom technique gives 94.9 kcal/mol.[17]

The value of 98 kcal/mol for $DH°_{298}(CH_3COCH_2\text{–}H)$ means that the stabilization energy in the acetonyl radical is zero. In terms of valence-bond theory, the resonance stabilization in radicals is due to simple delocalization of the unpaired electron, and the absence of stabilization energy in the acetonyl radical has been previously explained[7] as being due to the energy difference between the various canonical forms of the radical. Since the C–O π-bond energy in acetone is 78 kcal/mol[10b,16] and the C–C π-bond energy in isobutylene is 58 kcal/mol,[16] then in the following hypothetical structures of the acetonyl radical, ii should be 20 kcal/mol less stable than i.



i ii

In terms of valence-bond structures[18] it may be seen that the net change caused by delocalizing the C–O π bond would be −10 kcal/mol. The net change in



the case of the allyl radical is zero.[2b]

The stabilization energy in the methylacetonyl radical was estimated as 2.7 kcal/mol[8] and the difference between acetonyl and methylacetonyl may be explained on the same basis as the difference between allyl and methylallyl.[2b] That is, the methyl group stabilizes the partial charge at the secondary carbon atom by an "inductive" effect.

The important conclusion to be drawn from the values for the stabilization energies in β-carbonyl radicals is that a concerted mechanism must make a significant contribution to the decompositions of cyclobutyl ketones. Solly, Golden, and Benson[8] have shown that if methyl cyclobutyl ketone is assumed to decompose equally by a biradical process and a concerted process then the calculated stabilization energy in methylacetonyl is consistent with the above value.

The measured value of $DH°_{298}(CH_3COCH_2\text{–}H) = 98.3 \pm 1.8$ kcal/mol is consistent with $DH°_{298}(C_2H_5\text{–}H) = 98 \pm 1$ kcal/mol.[2b,5] Moreover, we have also found[19] that under the same experimental conditions, ethane brominates faster than acetone by an almost constant factor of ~4 over the temperature range of this investigation. Thus, for

$$Br + C_2H_6 \xrightarrow{1'} C_2H_5 + HBr$$

$\log k_1' = 11.6 - 14.0/\theta$ compared to $\log k_1 = 11.0 - 13.9/\theta$. Since the reaction symmetry is the same in both cases, the difference in A factors may be the result of slight structural differences in the respective transition-state complexes.

The A factor may be expressed in terms of collision theory as

$$A = pZe^{1/2}$$

where p is a steric factor, generally less than unity, and Z is the collision frequency. The $e^{1/2}$ term arises as a result of the $T^{1/2}$ dependence in Z. At $T_m = 576$°K, and with a mean collision diameter of 4.9 Å,[20]

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(14) B. G. Tucker and E. Whittle, *Trans. Faraday Soc.*, 61, 866 (1965); J. C. Amphlett and E. Whittle, *ibid.*, 62, 1662 (1966).

(15) G. C. Fettis and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 3037 (1961).

(16) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(17) S. Furuyama, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, 2, 83 (1970).

(18) K. W. Egger and S. W. Benson, *J. Amer. Chem. Soc.*, 88, 241 (1966).

(19) K. D. King, D. M. Golden, and S. W. Benson, *Trans. Faraday Soc.*, in press.

(20) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1954.

log $Ze^{1/2}$ (reaction 1) = 11.66, whereas log $Ze^{1/2}$ (reaction 1′) = 11.65.[19] Thus, collision theory does not explain why $A_1 < A_1'$, but the implication is that for reaction 1 there might be more need for orientation in the collision pair. In view of the structural differences between acetone and ethane this conclusion is reasonable.

According to transition-state theory the A factor for a bimolecular reaction is given by (standard state unit concentration)

$$A = (e^2kT/h)\exp[(\Delta S^{\ddagger}_{\mathrm{tr}} + \Delta S^{\ddagger}_{\mathrm{rot}} + \Delta S^{\ddagger}_{\mathrm{vib}})/R]$$

where the $\Delta S^{\ddagger}$'s are the translational, rotational, and vibrational entropies of activation, respectively. The evaluation of the $\Delta S^{\ddagger}$'s for bromine atom reactions has been discussed[19,21] and we have estimated[19] log $A_{1'}$ = 11.7 (T_m = 550°K). Applying the same principles as before, we estimate that log A_1 = 10.9 (550°K), in good agreement with the experimental result. The difference between $A_{1'}$ and A_1 is essentially due to a decrease in $\Delta S^{\ddagger}_{\mathrm{tr}} + \Delta S^{\ddagger}_{\mathrm{rot}}$ as RH increases in size from C_2H_6 to CH_3COCH_3 without complete compensation by the increase in $\Delta S^{\ddagger}_{\mathrm{vib}}$, as is usually the case.[21] Changes in internal rotation make a small contribution to the overall difference at the reaction temperature since the CH_3–CH_3 rotational barrier is 2.9 kcal/mol[16] and the CH_3–$COCH_3$ barrier is 0.8 kcal/mol.[16]

In the above calculations, the two bending and two rocking modes associated with the Br and transferring H atoms were assigned vibrations of ~250 cm^{-1} each. Although the agreement between calculated and experimental A factors is extremely good, these frequencies seem to be too low for what are essentially hydrogen atom motions. Moreover, in the calculations of Fettis, Knox, and Trotman-Dickenson,[21] where the two rocking modes were ignored, the bending frequencies were assigned extremely low values of <100 cm^{-1}. Of course, all of these calculations are based on a linear[22] configuration for C–H–Br in the transition-state complex. However, should the configuration be bent then major contributions to $\Delta S^{\ddagger}_{\mathrm{vib}}$ would be due to internal rotations of R in the R–H–Br complex and the bending modes may be assigned much higher frequencies.

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(21) G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 4177 (1960); G. C. Fettis and J. H. Knox, *Progr. React. Kinet.*, 2, 2 (1964).

(22) D. J. Wilson and H. S. Johnston, *J. Amer. Chem. Soc.*, 79, 29 (1957).

Kinetics of Hydrogen–Deuterium Exchange in Poly(N-vinylacetamide) Measured by Infrared Spectroscopy

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Abstract: The hydrogen–deuterium exchange in D_2O solutions of poly(N-vinylacetamide) has been studied as a function of pD at four temperatures. The rate constants observed for the exchange of the hydrogen atoms of the amide groups of the polymer are lower by a factor of ~20 than the corresponding exchange rate constants of N-methylacetamide. The interpretation of this observation is discussed and, as a likely explanation of the result, it is suggested that fast fluctuations of the conformation of the dissolved polymer molecules occur, and that the amide groups of the polymer are protected from solvent exposure for about 95% of the time.

Hydrogen atoms attached to electronegative atoms in groups such as –COOH, –NH_2, –OH, –SH, and –CONH– are known to be labile; when compounds containing such groups are dissolved in water, an exchange of hydrogen atoms takes place between the groups and the solvent. Measurements of the rate of this exchange in aqueous protein solutions are being used as a tool in studies of protein conformations.[2,3] It is quite generally observed that part of the hydrogen atoms in protein molecules exchanges with those of solvent water at considerably slower rates than do corresponding hydrogen atoms in low molecular weight compounds or in randomly coiled polypeptides.

It has been a basic assumption, underlying many studies of the hydrogen exchange, that this reduced reactivity of hydrogen atoms in protein molecules is characteristic of the conformation of the proteins, and, therefore, that measurements of the exchange rates may contribute to the elucidation of the nature of protein conformations. It was, however, pointed out by Klotz and coworkers,[2b,4,5] and also discussed in ref 2a, that a slow exchange in aqueous solutions might be explained partly or entirely by a change in the structure of the water surrounding the dissolved molecules, and that a more extensive investigation of the exchange in solutions of molecules simpler than proteins is needed before any definite conclusions can be drawn about the interpretation of the slow exchange in protein

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(1) Israel Institute for Biological Research, Ness-Ziona, Israel.

(2) (a) Aa. Hvidt and S. O. Nielsen, *Advan. Protein Chem.*, 21, 287 (1966); (b) I. M. Klotz, *J. Colloid Interface Sci.*, 27, 804 (1968).

(3) F. S. Parker and K. R. Bhaskar, *Appl. Spectrosc. Rev.*, 3, 91 (1969).

(4) H. Leichtling and I. M. Klotz, *Biochemistry*, 5, 4026 (1966).

(5) J. S. Scarpa, D. D. Mueller, and I. M. Klotz, *J. Amer. Chem. Soc.*, 89, 6024 (1967).